

O.104450/EH/AB
010829

PATENT APPLICATION

PCT/EP00/01837 (00.03.03)

APPLICANT: BIOTEC ASA
N-STRANDGT. 3
9008 TROMSØ
NORWAY

TITLE: "Cosmetic preparations"

COSMETIC PREPARATIONS

The field of the invention

The invention belongs to the field of cosmetics and concerns preparations, especially for the treatment of the skin and hair, which contain a synergistic mixture of specific water soluble β -glucans and chitosans, as well as the use of the mixtures for the production of cosmetic materials.

Prior art

The formation of wrinkles caused by increasing age is induced through the degradation of different macro molecules such as for example elastin and collagen, which are responsible for the elastases. Many inflammatory skin diseases, such as for example psoriasis or UV erythema, can also be causatively be linked to an increased concentration of serine proteases, such as e.g. elastase in the upper skin areas [see R.Voegeli et al. in *Cosm. Toil.* 111, 51(1996)].

The formation of wrinkles i the skin is normally not counteracted by means of physiological active principles, but by means of cosmetic agents. Many so-called "anti-ageing products" contain liposomes loaded with water or aqueous active agents, which through the fat layer of the skin are reaching the epidermis, where they gradually dissolve and through continuous water release compensate the skin recesses and regulate the moisture content of the skin. However, this effect is no combat against the causes, but only has a so-called "repair effect", which lasts only lasts for a short period of time. Also the use of specific polysaccharides as agents against the skin ageing is known from prior art. Thus it has been suggested in the patent US 5,223,491 to employ a carboxymethylated β -1,3 glucan, which had been extracted from the yeast fungus *Saccharomyces cerevisiae*, for topical application. The glucan is, however, insoluble in water and can accordingly only be formulated with much difficulties. From the European patent EP-B1 0500718 (Donzis) is further the use of water insoluble β -(1,3) glucans, which are obtained from the cell walls of yeast, known for revitalization of the skin. Finally, in WO 98/40082 (Henkel) the use of water soluble β -(1,3) glucans als active agents for the treatment of the skin have been proposed. But also these glucans, which preferably are schizopyhallan or krestin, i.e. extracts of fungi, have in practice not shown to be sufficiently effective.

The task of the present invention was therefore to make available novel cosmetic agents, which distinguish themselves in the field of skin treatment through an improved vitalization. Especially skin ageing, formation of wrinkles and skin roughness should be improved.

5

Description of the Invention

The object of the invention are cosmetic preparations, containing

- (a) water soluble β -(1,3) glucans, substantially free from β -(1,6) linkages, and
- 10 (b) chitosans.

Surprisingly it was found, that the addition of chitosans increases the skin vitalizing properties of specific β -(1,3) glucans in a synergistic way, while conversely the specific β -(1,3) glucanes definitive improve the film forming

15 properties of chitosans. In this manner it is possible especially to produce agents for skin and hair treatments, but also agents for sun protection with special performance properties.

Water soluble β -(1,3) glucans

20 The term glucans is intended to mean homopolysaccharides based on glucose. Depending on sterical linking there is a difference between β -(1,3), β -(1,4) and β -(1,6) glucans. β -(1,3) Glucans normally show a helical structure, whereas glucans with a (1,4) linkage generally have a linear structure. The β -glucans of the invention have a (1,3) structure, i.e. they are substantillay free

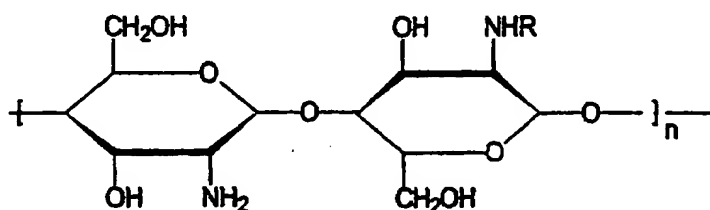
25 from undesired (1,6) linkages. Preferably such β -(1,3) glucans are used where the side chains exclusively show (1,3) linkages. Especially the agents contain glucans which are obtained on the basis of yeast from the family *Sacchaomyces*, especially *Saccharomyces cerevisiae*. Glucans of this type are available in technical amounts according to known methods. The international patent

30 application WO 95/30022 (Biotec-Mackzymal) describes e.g. a method for producing such substances, wherein glucans with β -(1,3) and β -(1,6) linkages are brought in contact with β -(1,6) glucanases in such a way, that practically all β -(1,6) linkages are loosened. Preferably used for the manufacture of these glucans are glucanases based on *Trichoderma harzianum*. As to the manufacture

and availability of the glucans contained in these agents, reference is made to the above cited publication.

Chitosans

- 5 Chitosans are biopolymers and belong to the group of hydrocolloids. From a chemical point of view they are partial deacetylated chitins with different molecular weights, and contain the following - idealized - monomer module:



- 10 In contrast to most of the hydrocolloids, which are negatively charged in the range of biological pH-values, chitosans are under these conditions cationic biopolymers. The positively charged chitosans can interact with opposite charged surfaces and are therefore used in cosmetic hair and body care agents as well as in pharmaceutical preparations (see *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed., vol. A6, Weinheim, Verlag Chemie, 1986, p. 231-332). A
- 15 summary of these subjects are also published in for example B. Gesslein et al., *HAPPI* 27, 57 (1990), O. Skaugrud in *Drug Cosm. Ind.* 148, 24 (1991) and E. Onsoyen et al. in *Seifen-Öle-Fette-Wachse* 117, 633 (1991). By the production of chitosan chitin is used as starting material, preferably the shell residues of crust animals, which are available in large amounts as cheap raw materials. The chitin
- 20 is thereby, using a method which first was described by Hackmann et al., usually first deprotonated by addition of bases, demineralized by addition of mineral acids and at last deacetylated by addition of strong bases, whereby the molecular weights can be distributed over a broad spectrum. Corresponding methods are for example known from *Makromol. Chem.* 177, 3589 (1976) or the French patent
- 25 application FR-A1 2701266. Preferably use is made of such types which are described in the German patent applications DE-A1 4442987 and DE-A1 19537001 (Henkel), and which have an average molecular weight of 10 000 to 2 500 000, preferably 800 000 to 1 200 000 Daltons, a viscosity according to Brookfield (1 % by weight in glycolic acid) below 5 000 mPas, a degree of

deacetylation in the range of 80 to 88 % and a content of ashes of less than 0,3 % by weight. In addition to the chitosans as typical cationic biopolymers come according to the invention also in question anionic, respectively nonionic derivatized chitosans, such as e.g. carboxylation, succinilation or alkoxylation products, as they are described for example in the German patent DE-C2 3713099 (L'Oreal) as well as in the German patent application DE-A1 19604180 (Henkel).

In a preferable embodiment of the invention, the preparations contain

- (a) 0,01 to 25, preferably 0,5 to 20 and especially 1 to 5 % by weight of water soluble β -(1,3) glucans, which are substantially free from β -(1,6) linkages, and
- (b) 0,01 to 5, preferably 0,5 to 3 and especially 1 to 2 % by weight of chitosans,

provided that the used amounts together with water and possibly other auxiliary and additional substances summarize to 100 % by weight.

Commercial applicability

The addition of chitosans leads to a synergistic increase in the skin vitalizing properties and film forming properties of glucans. A further object of the present invention concerns the use of mixtures which contain

- (a) water soluble β -(1,3) glucans, which are substantially free from β -(1,6) linkages, and
- (b) chitosans,

for production of cosmetic preparations, especially care and cleaning agents for skin and hair, as well as sun protection agents.

The preparations according to the invention, such as e.g. hair shampoos, hair lotions, foam baths, sun protection agents, lotions or cremes for face and body care, baby care products, decorative cosmetics, gels or ointments and suchlike can further as additional auxiliary or additional substances contain mild surfactants, oil bodies, emulsifiers, hyperfating agents, pearl lustre waxes, consistency substances, thickening agents, polymers, silicon compounds, fats, waxes, stabilizing agents, biogenic active substances, deodorants, agents against dandruff, film forming agents, swelling agents, UV light protection factors, antioxidants, inorganic colour pigments, hydrotropes, preservatives, insect

repellents, self tanning agents, solubilizing agents, perfume oils, colouring agents and suchlike.

Typical examples of suitable mild, i.e. especially skin compatible **surfactants**, are fatty alcohol polyglycol ether sulphates, monoglyceride sulphates, mono- and/or dialkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid glutamates, α -olefine sulphonates, ethercarboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkylamido betaines and/or protein fatty acid condensates, the last mentioned preferably based on wheat proteins.

As **oil bodies** use can be made of for example Guerbet alcohols based on fatty alcohols with 6 to 18, preferably 8 to 10 carbon atoms, esters of linear C_6 - C_{22} fatty acids with linear C_6 - C_{22} fatty alcohols, esters of branched C_6 - C_{13} carboxylic acids with linear C_6 - C_{22} fatty alcohols, such as e.g. myristyl myristate, myristyl palmitate, myristyl stearate, myristyl isostearate, myristyl oleate, myristyl behenate, myristyl erucate, cetyl myristate, cetyl palmitate, cetyl stearate, cetyl isostearate, cetyl oleate, cetyl behenate, cetyl erucate, stearyl myristate, stearyl palmitate, stearyl stearate, stearyl isostearate, stearyl oleate, stearyl behenate, stearyl erucate, isostearyl myristate, isostearyl palmitate, isostearyl stearate, isostearyl isostearate, isostearyl oleate, isostearyl behenate, isostearyl oleate, oleyl myristate, oleyl palmitate, oleyl stearate, oleyl isostearate, oleyl oleate, oleyl behenate, oleyl erucate, behenyl myristate, behenyl palmitate, behenyl stearate, behenyl isostearate, behenyl oleate, behenyl behenate, behenyl erucate, erucyl myristate, erucyl palmitate, erucyl stearate, erucyl isostearate, erucyl oleate, erucyl behenate and erucyl erucate. In addition esters of linear C_6 - C_{22} fatty acids with branched alcohols, especially 2-ethylhexanol, esters of hydroxycarboxylic acids with linear or branched C_6 - C_{22} fatty alcohols, especially dioctyl malate, esters of linear and/or branched fatty acids with polyvalent alcohols (such as e.g. propylene glycol, dimeric diol or trimeric triol) and/or Guerbet alcohols, triglycerides based on C_6 - C_{10} fatty acids, liquid mixtures of mono-/di-/triglycerides based on C_6 - C_{18} fatty acids, esters of C_6 - C_{22} fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, especially benzoic acid, esters of C_2 - C_{12} dicarboxylic acids with linear or branched alcohols with 1 to 22 carbon atoms or polyols with 2 to 10 carbon atoms and 2 to 6 hydroxyl groups, plant oils, branched primary alcohols, substituted cyclohexanes, linear and branched C_6 - C_{22} fatty

alcohol carbonates, Guerbet carbonates, esters of benzoic acid with linear and/or branched C₆-C₂₂ alcohols (e.g. Finsolv[®] TN), linear or branched, symmetrical or unsymmetrical dialkyl ethers with 6 to 22 carbon atoms in each alkyl group, ring opening products of epoxydated fatty acid esters with polyols, silicone oils and/or
5 aliphatic or naphthenic hydrocarbons, such as e.g. squalan, squalen or dialkyl cyclohexanes, can be used

As **emulsifiers** for example nonionic surfactants from at least one of the following groups may be used:

- 10 (1) Addition products of 2 to 30 moles ethylene oxide and/or 0 to 5 moles propylene oxide on linear fatty alcohols with 8 to 22 C atoms, on fatty acids with 12 to 22 C atoms and on alkyl phenols with 8 to 15 C atoms in the alkyl group;
- (2) C_{12/18} fatty acid mono- and -diesters of addition products of 1 to 30 moles ethylene oxide and glycerol;
- 15 (3) glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids with 6 to 22 carbon atoms and their ethylene oxide addition products;
- (4) alkyl mono- and oligoglycosides with 8 to 22 carbon atoms in the alkyl group and their ethoxylated analogues;
- 20 (5) addition products of 15 to 60 moles ethylene oxide on ricinus oil and/or hardened ricinus oil;
- (6) polyol and especially polyglycerol esters, such as e.g. polyglycerol polyricinoleate, polyglycerol poly-12-hydroxystearate or polyglycerol dimerate isostearate, and also mixtures of compounds from more of these classes of
25 substances;
- (7) addition products of 2 to 15 moles ethylene oxide on ricinus oil and/or hardened ricinus oil;
- (8) partial esters based on linear, branched, unsaturated or saturated C_{6/22} fatty acids, ricinolic acid and 12-hydroxy stearic acid and glycerol, polyglycerol,
30 pentaerythrite, dipentaerythrite, sugar alcohols (e.g. sorbitol), alkyl glucosides (e.g. methyl glucoside, butyl glucoside, lauryl glucoside) as well as polyglucosides (e.g. cellulose);
- (9) mono-, di- and trialkylphosphates as well as mono-, di- and/or tri-PEG alkylphosphates and their salts;

(10) wool wax alcohols;

(11) polysiloxane/polyalkyl/polyether copolymers or corresponding derivatives;

(12) mixed esters of pentaerythrite, fatty acids, citric acid and fatty alcohol

according to DE 1165574 PS and/or mixed esters of fatty acids with 6 to 22

5 carbon atoms, methyl glucose and polyols, preferably glycerol or polyglycerol,

(13) polyalkylene glycols, as well as

(14) glycerol carbonate.

The addition products of ethylene oxide and/or of propylene oxide on fatty
10 alcohols, fatty acids, alkyl phenols, glycerol mono- and diesters as well as sorbitan mono- and -diesters of fatty acids or on ricinus oil are known products which are commercially available. They are mixtures of homologous substances, with average degree of alkoxylation corresponding to the ratio of the amounts of the substances ethylene oxide and/or propylene oxide and substrate, with which
15 the addition reaction is carried out. C_{12/18} fatty acid mono- and -diesters of addition products of ethylene oxide on glycerol are known from DE 2024051 PS as revertive fattening agents for cosmetic preparations.

C_{8/18} alkyl mono- and oligoglycosides, their manufacture and their use is known from prior art. Their preparation can especially be carried out by reaction of
20 glucose or oligosaccharides with primary alcohols having 8 to 18 C atoms. With regard to the glycoside residue both monoglycosides, where a cyclic sugar group is glycosidically bonded to the fatty alcohol, and oligomeric glycosides with a degree of oligomerization until preferably about 8, are suitable. The degree of oligomerization is then a statistical mean value, based on a distribution of
25 homologues which is usual for such products of technical quality.

Zwitterionic surfactants can also be used as emulsifiers. The term zwitterionic surfactants is intended to mean such surface active compounds which in their molecule have at least a quaternary ammonium group and at least one carboxylate and one sulphonate group. Especially suitable zwitterionic surfactants
30 are the so-called betaines such as the N-alkyl-N,N-dimethyl ammonium glycinate, for example the coco alkyldimethyl ammonium glycinate, N-acylaminoethyl-N,N-dimethyl ammonium glycinate, for example the coco acylaminoethyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-hydroxyethyl imidazoline with in each case 8 to 18 C atoms in the alkyl or acyl -

groups, as well as the coco acylaminoethyl hydroxyethylcarboxymethyl glycinate. Especially preferred is that under the CTFA term *cocamidopropyl betaine* known fatty acid amide derivative. Also suitable emulsifiers are ampholytic surfactants. Ampholytic surfactants are such surface active compounds which in addition to a

5 C_{8/18} alkyl or acyl group in the molecule at least contain a free amino group and at least one -COOH or -SO₃H group and which can form inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyltaurines, N-alkylsarcosines,

10 2-alkylaminopropionic acids and alkylamino acetic acids with in each case about 8 to 18 C atoms in the alkyl group. Especially preferable ampholytic surfactants are the N-coco alkylamino propionate, the coco acylamino ethylaminopropionate and the C_{12/18} acylsarcosine. In addition to the ampholytic, also quaternary emulsifiers can be used, of which ester salts of the type of esterquats, preferably

15 methylquaternised di-fatty acid triethanolamine ester salts, are especially preferable.

As **hyperfating** agents substances such as for example lanolin and lecithin as well as polyethoxylated or acylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides can be used,

20 whereby the last mentioned at the same time act as foam stabilisers.

As exemplary **pearl gloss waxes** the following should be mentioned: Alkylene glycolester, especially ethyleneglycol distearate; fatty acid alkanolamides, especially coco fatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polyvalent, possibly

25 hydroxysubstituted carboxylic acids with fatty alcohols with 6 to 22 carbon atoms, especially long chain esters of tartaric acid; fat substances, such as for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates, wherein the sum of carbon atoms is at least 24, especially lauron and distearylether; fatty acids such as stearic acid, hydroxystearic acid or behenic

30 acid, ring opening products of olefine epoxides with 12 to 22 carbon atoms with fatty alcohols with 12 to 22 carbon atoms and/or polyols with 2 to 15 carbon atoms and 2 to 10 hydroxyl groups as well as their mixtures.

As **consistency givers** preferably use is made of fatty alcohols or hydroxy fatty alcohols with 12 to 22 and preferably 16 to 18 carbon atoms and additionally

partial glycerides, fatty acids or hydroxy fatty acids. A combination of these substances with alkyl oligoglucosides and/or fatty acid-N-methyl glucamides with the same chain length and/or polyglycerol-poly-12-hydroxy stearates.

Suitable **thickening agents** are for example types of aerosil (hydrophilic silicic acids), polysaccharides, especially xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethyl celluloses and hydroxyethyl celluloses, as well as higher molecular polyethylenglycol mono- and diesters of fatty acids, polyacrylates, (e.g. Carbopols® from Goodrich or Synthalenes® from Sigma), polyacrylamides, polyvinyl alcohol and polyvinyl pyrrolidone, surfactants such as for example ethoxylated fatty acid glycerides, ester of fatty acids with polyols such as for example pentaerythrite or trimethylolpropane, fatty alcohol ethoxylates with narrow distribution of homologous or alkyl oligoglucosides as well as electrolytes such as sodium chloride and ammonium chloride.

Suitable **cationic polymers** are for example cationic cellulose derivatives, such as e.g. a quaternized hydroxyethyl cellulose, which is available under the name of Polymer JR 400® from Amerchol, cationic starch, copolymers of diallyl ammonium salts and acrylamides, quaternized vinylpyrrolidone/vinylimidazol polymers, such as e.g. Luviquat® (BASF), condensation products of polyglycols and amines, quaternized collagen polypeptides, such as for example lauryl dimonium hydroxypropyl hydrolyzed collagen (Lamequat® L / Grünau), quaternized wheat polypeptides, polyethyleneimine, cationic silicone polymers, such as e.g. amidomethicones, copolymers of adipic acid and dimethylamino hydroxypropyl diethylenetriamine (Cartaretine® / Sandoz), copolymers of acrylic acid with dimethyl diallylammonium chloride (Merquat® 550 / Chemvicon), polyamino polyamides, such as e.g. described in FR 2252840 A, as well as their cross-linked water soluble polymers, cationic chitin derivatives such as for example quaternized chitosan, possibly micro crystalline distributed, condensation products of dihalogen alkyls, such as e.g. dibromobutane with bisdialkylamines, such as e.g. bis-dimethylamino-1,3-propane, cationic guar-gum, such as e.g. Jaguar® CBS, Jaguar® C-17, Jaguar® C-16 from Celanese, quaternised ammonium salt polymers, such as e.g. Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1 from Miranol.

As exemplary **anionic, zwitterionic, amphoteric and non-ionic polymers** the following can be used: Vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl

acrylate copolymers, methyl vinyl ether/maleic acid anhydride copolymers and their esters, non-cross-linked and with polyols cross-linked polyacrylic acids, acrylamido propyltrimethyl ammonium chloride/acrylate copolymers, octylacrylamide/methyl methacrylate/ tert.-butylaminoethyl methacrylate/2-
5 hydroxypropyl methacrylate copolymers, polyvinylpyrrolidone, vinylpyrrolidone/ vinylacetate copolymers, vinylpyrrolidone/ dimethylamino ethylmethacrylate/vinyl caprolactam terpolymers as well as possibly derivatized cellulose ethers and silicones.

Suitable **silicon compounds** are for example dimethyl polysiloxane, methylphenyl polysiloxane, cyclic silicones as well as amino, fatty acid, alcohol, polyether, epoxy, fluorine, glycoside and/or alkyl modified silicon compounds, which at room temperature can be in the liquid as well as in the resin state. Further suitable are simethicones, which are mixtures of dimethicones with an average chain length of 200 to 300 dimethyl siloxane units and hydrogenated silicates. A
15 detailed survey of suitable volatile silicones can also be found in Todd et al., *Cosm.Toil.* 91, 27 (1976).

Typical exemplary **fats** are glycerides, and as **waxes** natural waxes among others, can be used, such as e.g. candelilla wax, carnauba wax, Japan wax, espartogras wax, cork wax, guaruma wax, rice seed oil wax, sugar cane wax, ouricury wax, montan wax, beeswax, schellak wax, spermaceti, lanolin (wool wax), bürzel fat, ceresin, ozokerit (terrestrial wax), petrolatum, paraffin waxes, micro waxes; chemically modified waxes (hard waxes), such as e.g. montanester waxes, sasot waxes, hydrogenated yoyoba waxes as well as synthetic waxes, such as e.g. polyalkylene waxes and polyethylene glycol waxes.

25 As **stabilizers** metal salts of fatty acids, such as e.g. magnesium, aluminium and/or zinc stearate or ricinoleate can be used.

As **biogenic active substances** should be understood for example tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, desoxy ribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, extracts of plants and
30 vitamin complexes.

As **deodorant agents** e.g. antiperspirants such as aluminium chlorohydrate come into question. This agent is in the form of colourless, hygroscopic crystals, which easily melt in air, and is obtained through evaporation

of solutions of aluminium chloride in water. Aluminium chlorohydrate is used for manufacturing of perspiration inhibiting and deodorising preparations and has probably its effect through the partial closure of the perspiratory gland by means of precipitation of proteins and/or polysaccharides [see *J. Soc. Cosm. Chem.* 24, 281 (1973)]. Under the trade name Locron® of Hoechst AG, Frankfurt/FRG, an aluminium chlorohydrate is for example on the market, which corresponds to the formula $[Al_2(OH)_5Cl] \cdot 2.5 H_2O$, and use of this is especially preferred (see *J. Pharm. Pharmacol.* 26, 531 (1975)). In addition to the chlorohydrates also aluminium hydroxylactates as well as acid aluminium/zirconium salts can be used.

As further deo active agents esterase inhibitors can be added. These are preferably trialkyl citrates such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and especially triethyl citrate (Hydagen® CAT, Henkel KGaA, Düsseldorf/FRG). The substances inhibit the enzyme activity and thereby reduce the formation of odours. Probably the free acid is thereby set free through the cleavage of the citric acid ester, and this acid lowers the pH value of the skin so much that the enzymes thereby are inhibited. Further substances which can be used as esterase inhibitors are sterol sulphates or phosphates, such as for example lanosterol, cholesterol, campesterol, stigmasterol and sitosterol sulphate or phosphate, Dicarboxylic acids and their esters, such as for example glutaric acid, glutaric acid monoethylester, glutaric acid diethylester, adipic acid, adipic acid monoethylester, adipic acid diethylester, malonic acid and malonic acid diethylester, hydroxycarboxylic acids and their esters, such as for example citric acid, malic acid, tartaric acid or tartaric acid diethylester. Antibacterial active substances, which influence the germ flora and kill sweat destroying bacteria or inhibit their growth, can also be contained in the pin preparations. Examples of this are chitosan, phenoxyethanol and chlorohexidin gluconate. Also 5-chloro-2-(2,4-dichlorophen-oxy)-phenol has shown to have an especially good effect, and this product is marketed under the trade name Irgasan® by Ciba-Geigy, Basel/CH.

As **anti dandruff** agents climbazol, octopirox and zinc pyrethion can be used. Useable **film formation** agents are for example chitosan, microcrystalline chitosan, quaternary chitosan, polyvinylpyrrolidon, vinylpyrrolidon/vinylacetate copolymers, polymers of the acrylic acids, quaternary derivatives of cellulose, collagen, hyaluronic acid or its salts and similar compounds. As **swelling agents** for aqueous phases montmorillonite, clay mineral substances, pemulen, as well

as alkylmodified Carbopol types (Goodrich) can be used. Further suitable polymers or swelling agents can be found in the survey of R.Lochhead in *Cosm.Toil.108*, 95 (1993).

UV light protection factors are e.g organic substances (light protection filters) which by room temperature are in liquid or crystalline form, and which are capable of absorbing ultraviolet radiation and to set free the received energy in the form of radiation with long wavelength, e.g. in the form of heat. UVB filters can be soluble in oils or in water. As oil soluble substances the following are mentioned as examples:

- 10 • 3-Benzyliden camphor, respectively 3-benzylidene norcamphor and the derivatives thereof, e.g. 3-(4-methylbenzylidene) camphor as described in EP-B1 0693471;
 - 4-aminobenzoic acid derivatives, preferably 4-(dimethylamino) benzoic acid 2-ethylhexylester, 4-(dimethylamino) benzoic acid 2-octylester and
15 4-(dimethylamino) benzoic acid amylester;
 - esters of cinnamonic acid, preferably 4-methoxy cinnamonic acid 2-ethylhexylester, 4-methoxy cinnamonic acid propylester, 4-methoxy cinnamonic acid isoamylester, 2-cyano-3,3-phenyl cinnamonic acid 2-ethylhexylester (octocrylene);
 - 20 • esters of salicylic acid, preferably salicylic acid 2-ethylhexylester, salicylic acid 4-isopropyl benzylester, salicylic acid homomenthylester;
 - derivatives of benzophenone, preferably 2-hydroxy-4-methoxy benzophenone, 2-hydroxy-4-methoxy-4'-methyl benzophenone, 2,2'-dihydroxy-4-methoxy benzophenone;
 - 25 • esters of benzalmalonic acid, preferably 4-methoxy benzmalonic acid 2-ethylhexyl ester,
 - triazine derivatives, such as e.g. 2,4,6-trianilino-(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine and octyltriazone, as described in EP A1 0818450;
 - propane-1,3-diones, such as e.g. 1-(4-tert.-butylphenyl)-3-(4'-methoxy-phenyl)-propane-1,3-dion;
 - 30 • ketotricyclo(5,2,1,0)-decane derivatives, as described in EP-B1 06945521.
- As water soluble substances the following can be mentioned:
- 2-Phenylbenzimidazol-5-sulphonic acid and the alkali, alkaline earth, ammonium, alkylammonium, alkanolammonium and glucammonium salts;

- sulphonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenon-5-sulphonic acid and their salts;
- sulphonic acid derivatives of 3-benzylidencamphen, such as e.g. 4-(2-oxo-3-bornylidenmethyl)-benzene sulphonic acid and 2-methyl-5-(2-oxo-bornyliden) sulphonic acid and their salts.

As typical UV-A filters especially derivatives of benzoyl methane comes in question, such as e.g. 1-(4'-tert.-butylphenyl)-3-(4'-methoxyphenyl)propane-1,3-dion, 4-tert.butyl-4'-methoxydibenzoyl-methane (Parsol 1789), or 1-phenyl-3-(4'-isopropylphenyl-propane-1,3-dion. The UV-A and UV-B filters can of course also be used in mixtures. In this case combinations of octocrylene or camphor derivatives with butyl methoxydibenzoylmethane are especially photosensitive.

In addition to the mentioned soluble substances also insoluble light protection pigments can be used for this purpose, i.e. fine disperse metal oxides or salts. Examples of suitable metal oxides are especially zinc oxide and titanium dioxide and in addition other oxides of iron, zirconium, silicon, manganese, aluminium and cerium, as well as their mixtures. As salts silicates (talk), barium sulphate or zinc stearate can be used. The oxides and salts are used in the form of the pigments for skin caring and skin protecting emulsions and decorative cosmetics. The particles should have an average diameter of less than 100 nm, preferably between 5 and 50 nm and especially between 15 and 30 nm. They can have a spherical shape, but particles can also be used which have an ellipsoidal form or else have a shape which differs from the spherical shape. In sun protecting agents preferably so-called micro or nano pigments are used. Preferably micronized zinc oxide is used. Further suitable UV light protection factors can be found in the survey by P.Finkel in *SÖFW-Journal* 122, 543 (1996).

In addition to the primary light protection substances also secondary light protection substances of the **antioxidant** type find use, which interrupt the photochemical reaction chain, which is initiated when UV radiation penetrates the skin. Typical examples of such are amino acids (e.g. glycine, histidine, tyrosine, tryptophan) and their derivatives, imidazoles (e.g. urocanic acid) and their derivatives, peptides such as D,L-carnosine, D-carnosine, L-carnosine and their derivatives (e.g. anserine), carotinoids, carotene (e.g. α -carotin, β -carotin, lycopene) and their derivatives, chlorogenic acid and its derivatives, liponic acid and its derivatives (e.g. dihydroliponic acid), aurothioglucose, propylthiouracil and

other thiols (e.g. thioredoxin, glutathion, cystein, cystin, cystamine and their glycosyl, n-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl, γ -linoleyl, cholesteryl and glyceryl esters) as well as their salts, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and their derivatives (esters, ethers, peptides, lipides, nucleotides, nucleosides and salts) as well as sulfoximine compounds (e.g. buthionin sulfoximines, homocystein sulfoximines, butionin sulfones, penta-, hexa-, hepta-thionin sufoximine) in very small compatible doses (e.g. pmol to μ mol/kg), further (metal) chelating agents (e.g. α -hydroxy fatty acids, palmitic acid, phytinic acid, lactoferrine), α -hydroxy acids (e.g. citric acid, lactic acid, malic acid), humin acid, gallic acid, gallic extracts, bilirubin, bifiverdin, EDTA, EGTA and their derivatives, unsaturated fatty acids and their derivatives (e.g. γ -linolenic acid, linolic acid, oleic acid), folic acid and their derivatives, ubichinon and ubichinol and their derivatives, vitamin C and derivatives (e.g. ascorbyl palmitate, Mg-ascorbyl phosphate, ascorbyl acetate), tocopheroles and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (vitamin A patmitate) as well as koniferyl benzoate of benzoe resin, rutinic acid and their derivatives, α -glycosylrutin, ferula acid, furfuryliden glucitol, carnosine, butylhydroxy toluene, butylhydroxy anisol, nordihydro guajak resin acid, nordihydro guajaret acid, trihydroxy butyrophenon, uric acid and their derivatives, mannose and its derivatives, super oxide dismutase, zinc and its derivatives (e.g. ZnO, ZnSO₄), selen and its derivatives (e.g. selen-methionin), stilbenes and their derivatives (e.g. stilben oxide, trans-stilben oxide) and the derivatives suitable according to the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of these mentioned active substances.

For improvement of the flow properties further **hydrotropes**, such as for example ethanol, isopropyl alcohol, or polyols can be used. Polyols which in this case can be used preferably have 2 to 15 carbon atoms and at least two hydroxyl groups. The polyols can further contain additional functional groups, especially amino groups, or be modified with nitrogen. Typical examples are:

- Glycerol;
- alkylen glycols, such as for example ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol as well as polyethylen glycols with an average molecular weight from 100 to 1 000 Daltons;

- oligoglycerol mixtures of technical quality with a self-condensation degree of 1.5 to 10, such as e.g. technical quality diglycerol mixtures with a diglycerol content of 40 to 50 % by weight;
- methyol compounds, such as especially trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythrite and dipentaerythrite;
- low alkyl glucosides, especially such with 1 to 8 carbons in the alkyl residue, such as for example methyl and butyl glucoside;
- sugar alcohols with 5 to 12 carbon atoms, such as for example sorbitol or mannit;
- sugars with 5 to 12 carbon atoms, such as for example glucose or saccharose;
- aminosugars, such as for example glucamine;
- dialcoholamines, such as diethanolamine or 2-amino-1,3-propanediol.

As **preservatives** for example phenoxyethanol, formaldehyde solution, parabene, pentanediol or sorbic acid as well as those mentioned in enclosure 6, parts A and B of the cosmetic regulation, are further classes of substances. As **insect repellents** N,N-diethyl-m-toluamide, 1,2-pentanediol or insect repellent 3535 come into question, as **self tanning agent** dihydroxyacetone is suited.

As **perfume oils** mixtures of natural and synthetic scent substances should be mentioned. Natural scent substances are extracts of flowers (lilies, lavender, roses, jasmin, neroli, ylang-ylang), stems and blades (geranium, patchouli, petitgrain), fruits (anis, coriander, caraway, juniper), fruit shells (bergamot, lemon, orange), roots (macis, angelica, celery, kardamon, costus, iris, calmus), wood (stone pine, sandel, guajac, cedar, rosewood), herbs and grass (tarragon, lemongrass, sage, thyme), needles and twigs (spruce, fir, pine, traipsed), resins and balsams (galbanum, elemi, benzoe, myrrh, olibanum, opoponax). Raw materials from animals are also possible, such as for example zibet and castoreum. Typical synthetic odour compounds are products from types of esters, ethers, aldehydes, ketones, alcohols and hydrocarbons. Odour compounds from types of esters are e.g. benzyl acetate, phenoxyethyl isobutyrate, p-tert.-butylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbonyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styrallyl propionate and benzyl salicylate. Benzylethyl ether belongs for example to the ethers, to the aldehydes e.g. the linear alkanals

with 8 to 18 carbon atoms, citral, citronellal, citronellyl oxyacetaldehyde, cyclamen aldehyde, hydroxy citronellal, lilial and bourgeonal, to the ketones e.g. the ionones, α -isomethyl ionon and methylcedryl ketone, to the alcohols anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenylethyl alcohol and
5 terpeneol; to the hydrocarbons mainly the terpenes and balsams belong. However, mixtures of different odour substances are preferred, which together give a pleasant smell. Also etheral oils with low volatility, which often are used as aroma components, are suited as perfume oils, e.g. sage oil, chamomile oil, carnation oil, melissa oil, mint oil, cinnamon leaf oil, limeflower oil, juniper berry oil, vetiver oil,
10 oliban oil, galbanum oil, labolanum oil and lavandin oil. Preferably used are bergamot oil, dihydromyrcenol, lilial, lyral, citronellol, phenylethyl alcohol, α -hexylcinnamon aldehyde, geraniol, benzylacetone, cyclamen aldehyde, linalool, boisambrene forte, ambroxane, indol, hedione, sandelice, lemon oil, mandarin oil, orangenoil, allylamyl glycolate, cyclovertal, lavandine oil, muskateller sage oil,
15 β -damascone, geranium oil bourbon, cyclohexyl salicylate, vertofix coeur, iso-E-super, fixolide NP, evemyl, iraiden gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillate, irotyl and floramate, alone or in mixtures.

As **colouring agents** such substances which are suited and approved for cosmetic purposes can be used, such as for example those mentioned in the
20 publication "*Kosmetische Färbemittel*" (cosmetic dyes) of the "*Farbstoffkommission der Deutschen Forschungsgemeinschaft*", published by Verlag Chemie, Weinheim, 1984, p. 81-106. These dyes are generally used in concentrations from 0.001 to 0.1 % by weight, based on the whole mixture.

Typical examples of **germ inhibiting** substances are preservatives with
25 specific effects against gram-positive bacteria, such as 2,4,4'-trichloro-2'-hydroxy diphenylether, chlorohexidin (1,6-di-(4-chlorophenyl-biguanido-hexan) or TCC (3,4,4'-trichlorocarbanilide). Many scent substances and etheral oils also have antimicrobial properties. Typical examples are the active agents eugenol, menthol and thymol in carnation, mint and thyme oil. An interesting natural deo substance
30 is the terpene alcohol farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol), which is present in lime flower oil and has a smell of lilies of the valley. Also glycerol monolaurate have been used as bacteriostaticum. Normally the content of the further germ inhibiting agent is about 0.1 to 2 % by weight - based on the solids content of the preparations.

The cumulative contents of the auxiliary and additional agents can be 1 to 50, preferably 5 to 40 % by weight, based on the agents. The manufacture of the agents can take place by common cold or hot processes; preferably the work is carried out according to the phase inversion temperature method.

5

Examples

10 A panel consisting of 15 female probands aged between 35 and 50 years were during a time period of 28 days daily exposed to a daily exposition of different glucans and/or chitosans. The probands used the skin cremes daily before going to bed. With intervals of 7 days the number, depth and lenght of the skin wrinkles were determined for each of the participants by means of profilometry of a selected part of the skin, i.e. a vertcal stripe of 2 cm width and 5
15 cm length, having an upper left and right boundary. which occurs if from the nose root a horizontal line is drawn, from this and against the right eye 2, respectively 4 cm, are cleared away and both resulting points in each case are elongated in an angle of 270° in each case 2 cm. The dimensionless product of depht, number and lenght of the skin wrinkles on the day before the beginning of the exposure
20 was set as standard (= 100 %), and all the following measurements were based on this. At the same time the skin roughness of the pro-bands was evaluated on a scale from 0 = "unchanged" to 3 = "strongly improved". The results are summarized in Table 1. Examples 1 and 2 are according to the invention, the examples V1 to V3 are for comparison.

25

Table 1**Skin ageing and skin roughness**

| Composition / Performance | 1 | 2 | V1 | V2 | V3 |
|----------------------------------|----------|----------|-----------|-----------|-----------|
| Cetyl stearyl alcohol | 8.0 | 8.0 | 8.0 | 8.0 | 8.0 |
| Ceteareth-12 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Ceteareth-20 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Cetearyl isononanoate | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 |
| Paraffin oil, viscous | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Baysilon oil M 300 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| β -1,3 Glucan * | 20.0 | 20.0 | 20.0 | - | - |
| Chitosan ** | 2.0 | - | - | 2.0 | - |
| Succinilated chitosan *** | - | 2.0 | - | - | 2.0 |
| Glycerol | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| Water ad 100 | | | | | |
| Skin ageing [%-rel] | | | | | |
| - bevor the treatment | 100 | 100 | 100 | 100 | 100 |
| - after 7 d | 91 | 92 | 96 | 99 | 99 |
| - after 14 d | 85 | 87 | 91 | 97 | 97 |
| - after 21 d | 80 | 83 | 85 | 95 | 95 |
| - after 28 d | 73 | 75 | 79 | 91 | 91 |
| Skin roughness | | | | | |
| - bevor the treatment | 0 | 0 | 0 | 0 | 0 |
| - after 7 d | 2 | 1 | 1 | 0 | 0 |
| - after 14 d | 3 | 2 | 2 | 0 | 0 |
| - after 21 d | 3 | 3 | 3 | 1 | 1 |
| - after 28 d | 3 | 3 | 3 | 1 | 1 |

*) Highcareene® GS

**) Hydagen® CMF

***) Hydagen® SCD (all are from Henkel KGaA, Düsseldorf/FRG)

The following table contains formulation examples.

Table 1 - Cosmetic Preparations (water, preservatives ad 100 % by weigh)

| Composition (INCI) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-----------------------------------------------------------------------------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|
| Texapon® NSO Sodium laureth. sulphate | - | - | - | - | - | - | 38.0 | 38.0 | 25.0 | - |
| Texapon® SB 3 Disodium laureth. sulphosuccinate | - | - | - | - | - | - | - | - | 10.0 | - |
| Plantacare® 818 Coco glucosides | - | - | - | - | - | - | 7.0 | 7.0 | 6.0 | - |
| Plantacare® PS 10 Sodium laureth.sulphate (and) coco glucosides | - | - | - | - | - | - | - | - | - | 16.0 |
| Dehyton® PK 45 Cocamidopropyl betaine | - | - | - | - | - | - | - | - | 10.0 | - |
| Dehyquart® A Centrimonium chloride | 2.0 | 2.0 | 2.0 | 2.0 | 4.0 | 4.0 | - | - | - | - |
| Dehyquart L® 80 Dicocoilmethylethoxyonium methosulphate (and) propylene glycol | 1.2 | 1.2 | 1.2 | 1.2 | 0.6 | 0.6 | - | - | - | - |
| Eumulgin® B2 Ceteareth-20 | 0.8 | 0.8 | - | 0.8 | - | 1.0 | - | - | - | - |
| Eumulgin® VL 75 Lauryl glucoside (and) polyglyceryl-2 polyhydroxy stearate (and) glycerol | - | - | 0.8 | - | 0.8 | - | - | - | - | - |
| Lanette® O Cetearyl alcohol | 2.5 | 2.5 | 2.5 | 2.5 | 3.0 | 2.5 | - | - | - | - |
| Cutina® GMS Glyceryl stearate | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 1.0 | - | - | - | - |
| Cetiol® HE PEG-7 glyceryl cocoate | 1.0 | - | - | - | - | - | - | - | 1.0 | - |
| Cetiol® PGL Hexyldecanol (and) hexyldecyl laurate | - | 1.0 | - | - | 1.0 | - | - | - | - | - |
| Cetiol® V Decyl oleate | - | - | - | 1.0 | - | - | - | - | - | - |
| Eutanol® G Octyldodecanol | - | - | 1.0 | - | - | 1.0 | - | - | - | - |
| Nutrilan® Keratin W Hydrolyzed keratine | - | - | - | 2.0 | - | - | - | - | - | - |
| Lamesoft® LMG Glyceryl laurate (and) potassium cocoyl hydrolyzed collagen | - | - | - | - | - | - | 3.0 | 2.0 | 4.0 | - |
| Euperlan® PK 3000 AM Glyceryl distearate (and) laureth.-4 (and) cocamidopropyl betaine | - | - | - | - | - | - | - | 3.0 | 5.0 | 5.0 |
| Generol® 122 N Soya sterol | - | - | - | - | 1.0 | 1.0 | - | - | - | - |
| Highcareen® GS Betaglucan | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Desoxy ribonucleic acid Molecular weight approx. 70000 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Copherol® 12250 Tocopherol acetate | - | - | 0.1 | 0.1 | - | - | - | - | - | - |
| Artypon® F Laureth-2 | - | - | - | - | - | - | 3.0 | 3.0 | 1.0 | - |
| Sodium chloride | - | - | - | - | - | - | - | 1.5 | - | 1.5 |

(1-4) Hair rinsing, (5-6) Hair cure, (7-8) Shower bath, (9) Shower gel, (10) Cleaning lotion

Table 1 Cosmetic preparations (water, preservatives ad 100 % by weight) - (cont.)

| Composition (INCI) | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|--------------------------------------------------------------------------------------------------|------|------|------|------|------|------|------|------|------|------|
| Texapon® NSO Sodium laureth. sulphate | 20.0 | 20.0 | 12.4 | - | 25.0 | 11.0 | - | - | - | - |
| Texapon® K 14 S Sodium myreth. sulphate | - | - | - | - | - | - | - | - | 11.0 | 23.0 |
| Texapon® SB 3 Disodium laureth. sulphosuccinate | - | - | - | - | - | 7.0 | - | - | - | - |
| Plantacare® 818 Coco glucosides | 5.0 | 5.0 | 4.0 | - | - | - | - | - | 6.0 | 4.0 |
| Plantacare® 2000 Decyl glucoside | - | - | - | - | 5.0 | 4.0 | - | - | - | - |
| Plantacare® PS 10 Sodium laureth. sulphate (and) coco glucosides | - | - | - | 40.0 | - | - | 16.0 | 17.0 | - | - |
| Dehyton® PK 45 Cocamidopropyl betaine | 20.0 | 20.0 | - | - | 8.0 | - | - | - | - | 7.0 |
| Eumulgin® B2 Cetareth-20 | - | - | - | 1.0 | 1.0 | - | - | - | - | - |
| Lameform® TGI Polyglyceryl-3 isostearate | - | - | - | 4.0 | - | - | - | - | - | - |
| Dehymuls® PGPH Polyglyceryl-2 dipolyhydroxy stearate | - | - | 1.0 | - | - | - | - | - | - | - |
| Monomuls® 90-L 12 Glyceryl laurate | - | - | - | - | - | - | - | - | - | 1.0 |
| Cutina® GMS Glyceryl stearate | - | - | - | - | - | - | - | - | 1.0 | - |
| Cetiol® HE PEG-7 Glyceryl cocoate | - | 0.2 | - | - | - | - | - | - | - | - |
| Eutanol® G Octyldodecanol | - | - | - | 3.0 | - | - | - | - | - | - |
| Nutrilan® Keratin W Hydrolyzed keratin | - | - | - | - | - | - | - | - | 2.0 | 2.0 |
| Nutrilan® I Hydrolyzed collagen | 1.0 | - | - | - | - | 2.0 | - | 2.0 | - | - |
| Lamesoft® LMG Glyceryl laurate (and) potassium cocoyl hydrolyzed collagen | - | - | - | - | - | - | - | - | 1.0 | - |
| Lamesoft® 156 Hydrogenated tallow glyceride (and) potassium cocoyl hydrolyzed collagen | - | - | - | - | - | - | - | - | - | 5.0 |
| Gludin® WK Sodium cocoyl hydrolyzed wheat protein | 1.0 | 1.5 | 4.0 | 1.0 | 3.0 | 1.0 | 2.0 | 2.0 | 2.0 | - |
| Euperlan® PK 3000 AM Glycol distearate (and) laureth-4 (and) cocamidopropyl betaine | 5.0 | 3.0 | 4.0 | - | - | - | - | 3.0 | 3.0 | - |
| Panthenol | - | - | 1.0 | - | - | - | - | - | - | - |
| Highcareen® GS Betaglucan | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Desoxy ribonucleic acid Molecular weight approx. 70000 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Arlyp n® F Laureth-2 | 2.6 | 1.6 | - | 1.0 | 1.5 | - | - | - | - | - |
| Sodium chloride | - | - | - | - | - | 1.6 | 2.0 | 2.2 | - | 3.0 |
| Glycerol (86 % by weight) | - | 5.0 | - | - | - | - | - | 1.0 | 3.0 | - |

(11-14) Shower bath "two-in-one". (15-20) Shampoo

Tabl 1 - Cosmetic preparations (water, preservatives ad 100 % by weight) - (cont. 2)

| Composition (INCI) | 21 | 22. | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|-------------------------------------------------------------------------------------------------------------|-----------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Texapon® NSO Sodium laureth. sulphate | - | 30.0 | 30.0 | - | 25.0 | - | - | - | - | - |
| Plantacare® 818 Coco glucosides | - | 10.0 | - | - | 20.0 | - | - | - | - | - |
| Plantacare® PS 10 Sodium laureth. sulphate (and) coco glucosides | 22.0 | - | 5.0 | 22.0 | - | - | - | - | - | - |
| Dehyton® PK 45 Cocamidopropyl betaine | 15.0 | 10.0 | 15.0 | 15.0 | 20.0 | - | - | - | - | - |
| Emulgade® SE Glyceryl stearate (and) ceteareth. 12/20 (and) cetearyl alcohol (and) cetylpalmitate | - | - | - | - | - | 5.0 | 5.0 | 4.0 | - | - |
| Eumulgin® B1 Ceteareth-12 | - | - | - | - | - | - | - | 1.0 | - | - |
| Lameform® TGI Polyglyceryl-3 isostearate | - | - | - | - | - | - | - | - | 4.0 | - |
| Dehymuls® PGPH Polyglyceryl-2 dipolyhydroxystearate | - | - | - | - | - | - | - | - | - | 4.0 |
| Monomuls® 90-O 18 Glyceryl oleate | - | - | - | - | - | - | - | - | 2.0 | - |
| Cetiol® HE PEG-7 Glyceryl cocoate | 2.0 | - | - | 2.0 | 5.0 | - | - | - | - | 2.0 |
| Cetiol® OE Dicaprylyl ether | - | - | - | - | - | - | - | - | 5.0 | 6.0 |
| Cetiol® PGL Hexyldecanol (and) hexyldecyl laurate | - | - | - | - | - | - | - | 3.0 | 10.0 | 9.0 |
| Cetiol® SN Cetearyl isononanoate | - | - | - | - | - | 3.0 | 3.0 | - | - | - |
| Cetiol® V Decyl oleate | - | - | - | - | - | 3.0 | 3.0 | - | - | - |
| Myritol® 318 Coco caprylate caprate | - | - | - | - | - | - | - | 3.0 | 5.0 | 5.0 |
| Bees Wax | - | - | - | - | - | - | - | - | 7.0 | 5.0 |
| Nutrilan® Elastin E20 Hydrolyzed elastin | - | - | - | - | - | 2.0 | - | - | - | - |
| Nutrilan® I-50 Hydrolyzed collagen | - | - | - | - | 2.0 | - | 2.0 | - | - | - |
| Gluadin® AGP Hydrolyzed wheat glutene | 0.5 | 0.5 | 0.5 | - | - | - | - | 0.5 | - | - |
| Gluadin® WK Sodium cocoyl hydrolyzed wheat protein | 2.0 | 2.0 | 2.0 | 2.0 | 5.0 | - | - | - | 0.5 | 0.5 |
| Eupertan® PK 3000 AM Glycol distearate (and) laureth-4 (and) cocamidopropyl betaine | 5.0 | - | - | 5.0 | - | - | - | - | - | - |
| Highcareen® GS Betaglucan | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Desoxy ribonucleic acid Molecular weight approx. 70000 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Magnesium sulphate heptahydrate | - | - | - | - | - | - | - | - | 1.0 | 1.0 |
| Glycer I (86 % by weight) | - | - | - | - | - | 3.0 | 3.0 | 5.0 | 5.0 | 3.0 |

(21-25) Foam bath, (26) Soft creme, (27.28) Moisture emulsion, (29.30) Night creme

Tabl 1 - Cosmetic preparations (water, preservatives ad 100 % by weight) - (cont. 3)

| Composition (INCI) | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
|-------------------------------------------------------------------------------------------------------|-----|-----|------|-----|-----|-----|-----|------|------|------|
| Dehymuls® PGPH Polyglyceryl-2 dipolyhydroxystearate | 4.0 | 3.0 | - | 5.0 | - | - | - | - | - | - |
| Lameform® TGI Polyglyceryl-3 diisostearate | 2.0 | 1.0 | - | - | - | - | - | - | - | - |
| Emulgade® PL 68/50 Cetearyl glucoside (and) cetearyl alcohol | - | - | - | - | 4.0 | - | - | - | 3.0 | - |
| Eumulgin® B2 Ceteareth-20 | - | - | - | - | - | - | - | 2.0 | - | - |
| Tegocare® PS Polyglyceryl-3 methylglucose distearate | - | - | 3.0 | - | - | - | 4.0 | - | - | - |
| Eumulgin VL75 Polyglyceryl-2 dipolyhydroxystearate (and) lauryl glucoside (and) glycerol | - | - | - | - | - | 3.5 | - | - | 2.5 | - |
| Beeswax | 3.0 | 2.0 | 5.0 | 2.0 | - | - | - | - | - | - |
| Cutina® GMS Glyceryl stearate | - | - | - | - | - | 2.0 | 4.0 | - | - | 4.0 |
| Lanette® O Cetearyl alcohol | - | - | 2.0 | - | 2.0 | 4.0 | 2.0 | 4.0 | 4.0 | 1.0 |
| Antaron® V 216 PVP / hexadecene copolymer | - | - | - | - | - | 3.0 | - | - | - | 2.0 |
| Myritol® 818 Coco glycerides | 5.0 | - | 10.0 | - | 8.0 | 6.0 | 6.0 | - | 5.0 | 5.0 |
| Finsolv® TN C12/15 Alkyl benzoate | - | 6.0 | - | 2.0 | - | - | 3.0 | - | - | 2.0 |
| Cetiol® J 600 Oleyl erucate | 7.0 | 4.0 | 3.0 | 5.0 | 4.0 | 3.0 | 3.0 | - | 5.0 | 4.0 |
| Cetiol® OE Dicaprylyl ether | 3.0 | - | 6.0 | 8.0 | 6.0 | 5.0 | 4.0 | 3.0 | 4.0 | 6.0 |
| Mineral Oil | - | 4.0 | - | 4.0 | - | 2.0 | - | 1.0 | - | - |
| Cetiol® PGL Hexadecanol (and) hexyl laurate | - | 7.0 | 3.0 | 7.0 | 4.0 | - | - | - | 1.0 | - |
| Panthenol / Bisabolol | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| Highcareen® GS Betaglucan | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Desoxy ribonucleic acid Molecular weight approx. 70000 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Copherol® F 1300 Tocopherol / tocopheryl acetate | 0.5 | 1.0 | 1.0 | 2.0 | 1.0 | 1.0 | 1.0 | 2.0 | 0.5 | 2.0 |
| Neo Heliopan® Hydro Sodium phenylbenzimidazole sulphonate | 3.0 | - | - | 3.0 | - | - | 2.0 | - | 2.0 | - |
| Neo Heliopan® 303 Octocrylene | - | 5.0 | - | - | - | 4.0 | 5.0 | - | - | 10.0 |
| Neo Heliopan® BB Benzophenone-3 | 1.5 | - | - | 2.0 | 1.5 | - | - | - | 2.0 | - |
| Neo Heliopan® E 1000 Isoamyl p-metoxycinnamate | 5.0 | - | 4.0 | - | 2.0 | 2.0 | 4.0 | 10.0 | - | - |
| Neo Heliopan® AV Octyl metoxycinnamate | 4.0 | - | 4.0 | 3.0 | 2.0 | 3.0 | 4.0 | - | 10.0 | 2.0 |
| Uvinul® T 150 Octyl triazone | 2.0 | 4.0 | 3.0 | 1.0 | 1.0 | 1.0 | 4.0 | 3.0 | 3.0 | 3.0 |
| Zinc oxide | - | 6.0 | 6.0 | - | 4.0 | - | - | - | - | 5.0 |
| Titanium dioxide | - | - | - | - | - | - | - | 5.0 | - | - |
| Glycerol (86 % by weight) | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |

(31) W/O Sun protection creme, (32-34) W/O Sun protection lotion, (35, 38,40) O/W Sun protection lotion (36, 37, 39) O/W Sun protection creme